

**PATENT ABSTRACTS OF JAPAN**(11)Publication number : **05-320358**(43)Date of publication of application : **03.12.1993**

(51)Int.Cl.

C08H 1/06

B44C 5/06

(21)Application number : **04-174659**(71)Applicant : **AJINOMOTO TAKARA CORP:KK**(22)Date of filing : **22.05.1992**(72)Inventor : **DATE TATSUYA  
ISHII AKIO****(54) KERATIN PROTEIN ARTICLE MOLDED BY HIGH-PRESSURE MOLDING**

(57)Abstract:

PURPOSE: To obtain a keratin protein molded article having excellent toughness, engraving suitability and feeling to finger and useful as artificial ivory, artificial tortoise shell, stamp material, etc., by compounding powdery keratin, etc., with a specific amount of a binder and molding the obtained composition under high pressure.

CONSTITUTION: The keratin protein molded article is produced by the high- pressure molding of a composition composed of (A) preferably 70-95wt.% of powdery or fibrous keratin having an average size of  $\geq 0.1\mu\text{m}$ , e.g. hoof, horn, beak, claw, scale, carapace, fwr, feather, wool or hair of birds and animals and (B) <50wt.% in total (based on the total composition) of arbitrary additives such as a binder (e.g. partially decomposed protein or gelatin), a cross-linking agent (e.g. epoxy resin), etc.

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

CLAIMS

---

[Claim(s)]

[Claim 1] A nature high voltage cast of keratin protein produced by carrying out high-pressure molding of the compound, comprising:

Powder or fibrous keratin.

It is the total quantity applied by request and they are less than 50% of the weight of a binder and other additive agents of the whole quantity.

[Claim 2] The cast according to claim 1 whose average size keratin is a thing of 0.1 micrometers or more for keratin powder or textiles, such as a hoof of wildlife, an angle, a beak, a nail, scales, a shell, animal hairs, feathers, wool, and the hair.

[Claim 3] A binder A protein partial decomposition product, gelatin, glue, collagen, casein, Milk, an egg white, starch, cystine, cystein, thioglycollate salt, fats and oils, A natural material and/or an epoxy resin which are chosen from rosin, sap, crude rubber (NR), etc., Melamine resin, urea resin, polyester resin, an acrylic resin, polyurethane resin, Polyamino resin, polycarbonate resin, polyvinyl chloride resin, polyamino acid resin, The cast according to claim 1 which are synthetic rubbers, such as a synthetic resin chosen from PVA, polyolefin resin, etc. and SBR (styrene butadiene rubber), IR (isoBURENGOMU), and BR (butadiene rubber).

[Claim 4] The cast according to claim 1 in which said additive agent is a cross linking agent.

[0001]

---

[Translation done.]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DETAILED DESCRIPTION**

---

[Detailed Description of the Invention]

[Field of the Invention] This invention relates to the denaturation particles produced by grinding high voltage casts, such as the keyboard of the artificial ivory, tortoiseshell, and piano which are produced by consisting of powder or fibrous keratin, or carrying out high-pressure molding of the compound which contains it as the main ingredients, a seal material, a decorative sheet, accessories, a tire, and a sheet, and this.

[0002]

[Description of the Prior Art] Although tortoiseshell, the angle of a water buffalo, ivory, etc. have been conventionally appointed by raw materials, such as a keyboard of a seal and a piano, and accessories, to a position of a trust, import and use of these natural materials are becoming difficult by social background change of international animal protection.

Development of those alternative raw materials and development of the studless tire tread etc. which solve the dust public nuisance by spike tire use are demanded.

[0003] As such alternative raw materials, to for example, methyl methacrylate resin, unsaturated polyester resin, etc. Magnesium hydroxide, The artificial ivory which hardened the husks of cast [ from what added inorganic fillers, such as aluminium hydroxide, titanium oxide, and calcium carbonate, ], or an egg from cow's milk casein is developed. However, neither of these raw materials attain to far the demand quality of making hydrophilic nature and hydrophobicity holding and satisfying robustness, sculpture nature, finger touch nature, etc.

[0004] Although it seems that the trial that what ground silk thread, wool, fowl feathers, etc. and was made powdered will be melted with an organic solvent, scleroprotein, such as keratin and collagen, will be extracted, I will consider it as the shape of a thin film, I will lay this also on top of many [-fold ] and I will obtain the substitute of tortoiseshell recently is also made, It seems that result still sufficient by research having just started has not been acquired.

[0005]

[Problem(s) to be Solved by the Invention] Then, it is the invention purpose to obtain molding process articles, such as artificial ivory produced by processing the cast raw material and it which have various physical properties, tactile feeling, sculpture processability, etc. which could not be attained for the conventional alternative raw material, a seal, a piano keyboard, and accessories made from BE \*\*\*\*.

[0006]

[Means for Solving the Problem] If this invention is followed, the above-mentioned invention purpose will be attained by nature high voltage cast of keratin protein produced with the total quantity applied by powder or fibrous keratin, and request by carrying out high-pressure molding of the compound which consists of less than 50% of the weight of BAINTA and other additive agents of the whole quantity.

[0007] In this invention, it consists of powder or fibrous keratin, or a compound which makes it the main ingredients is directly made with a cast by high-pressure molding, and the characteristic which a keratin raw material has essentially is used as it is.

[0008]Keratin used by this invention is powder or textiles, such as a hoof of wildlife, an angle, a beak, a nail, scales, a shell, animal hairs, feathers, wool, and the hair, and average size is 0.1 micrometers or more about several millimeters. it is used here -- average size -- a word -- granular material -- mean particle diameter -- fibrous material means the diameter of average length. These powder or textiles is obtained grinding or by carrying out frost shattering after remaining as it is or pretreatment in the above-mentioned natural material. (Japanese Patent Application No. No. 125661 [ three to ]).

[0009]these powder or fibrous keratin is independent, respectively -- it is -- it is used as two or more sorts of mixtures, and is used at 70 to 95% of the weight of a rate to full weight of a compound given to high-pressure molding more preferably to size and 100 % of the weight than 50 % of the weight. Since it may be hard to come out of intensity if it exceeds 95 % of the weight, it should consider even as 95 % of the weight by the purpose of use, and there is a tendency for a feeling of nature to be spoiled, on 50 or less % of the weight of another side.

[0010]A binder added by request A protein partial decomposition product, gelatin, glue, Casein, milk, an egg white, starch, cystine, cystein, thioglycollate salt, A natural material and/or an epoxy resin which are chosen from rosin, sap, crude rubber, etc., Melamine resin, urea resin, polyester resin, an acrylic resin, polyurethane resin, It is used in a form of one sort or two sorts or more of these mixtures by synthetic rubbers, such as a synthetic resin chosen from polyamino resin, polycarbonate resin, polyvinyl chloride resin, polyamino acid resin, polyolefin resin, etc. and SBR, IR, BR, CR, EPM, and EPDM.

[0011]Additive agents other than the above-mentioned ingredient, such as other resin publicly known as an arbitrary ingredient, a bulking agent, a color, paints, a reinforcing agent, a cross linking agent, and a catalyst, can be blended. However, it should carry out with the total quantity to less than 50% of the weight of all the compounds, otherwise a feeling of nature is spoiled, and quantity of these binders and an additive agent is not desirable.

[0012]In a desirable example, a little cross linking agents and a coupling agent are blended especially. As this cross linking agent, for example, 2, 4-tolylene diisocyanate prepolymer adduct object, An epoxy resin or a compound, a silane coupling agent, an organic metal coupling agent, Melamine, formalin, benzoguanamine, urea, thioglycollate salt, Cystein, fats and oils which have a double bond, etc. are used preferably, at the time of molding, crosslinking reaction is performed at a reaction with reactive functional groups, such as hydroxyl on the surface of keratin, carboxyl, and an amino group, and a cast excellent in special [ of robustness ] is obtained.

[0013]In this invention, the above-mentioned compound is directly made with a cast by high-pressure molding. Under the present circumstances, tangling between keratin particles or between textiles and a re-polymerization are performed simultaneously, and bridge construction is performed to keratin molecule comrade arbitration in existence of a cross linking agent. Ultra-high pressure molding methods, such as an isotropic pressure pressure method between method; \*\* (the WIP method) according [ high-pressure molding ] to a solid ultra-high pressure press for example, and an isotropic pressure pressure method between the colds (the CIP method); or although it carries out with high pressure forming, such as injection molding and compression molding, again, It is preferred to be especially based on maximum-pressure 10,000 kgf/cm<sup>2</sup>, a temperature-20-200 \*\* isotropic pressure pressure method between \*\* and 6,000 kgf/cm<sup>2</sup>, an isotropic pressure pressure method between the colds of a room temperature, and solid ultra-high pressure pressing method 10 ton/cm<sup>2</sup>.

[0014]Although it is usually preferred that a compound is used as uniform composition when fabricating, it is carried out by request also to an annual-rings stratified thing.

[0015]Molding useful in molding process things provided with outstanding appearance, feel, absorptivity, oil absorption property, robustness, and sculpture nature by this invention method, such as artificial ivory, seal material, a piano keyboard, accessories made from tortoiseshell, a decorative sheet, a printing material, and a tire, is obtained.

[0016]An example explains this invention below.

[Example 1] Seal material (artificial water buffalo angle)

\*\* \*\* W/W %\*\* \*\*\*\* impalpable powder 70.0\*\* cow bone powder 10.0\*\* epoxy resin (Epicoat 1004)



20.0 (97 \*\* of softening temperature granular material) Total 100.0[0017]The epoxy resin granular material 20g and the cow bone powder 10g were taught to a thunder Khai machine, and were ground for 1 hour. The \*\*\*\* [ this ] impalpable powder 70g was added, and it mixed uniformly. Having filled up a cylindrical mold with a deaerator 18 mm in inside diameter, and 150 mm in height with a part of this compound, and deaerating from the middle, application of pressure and temperature up were continued from the upper and lower sides, and it held at  $200 \text{ kg/cm}^2 \times 130$  \*\* for 2 hours. Obtained mold goods were removed from a metallic mold, and seal material fitness was evaluated.  
[0018]

第 1 表

	実施例 1	比較例 1 市販水牛角製	比較例 2 市販フェノール樹脂製
外 観	良	優	可
触 感	優	優	可
彫刻性	良	良	可
朱 肉 付着性	優	優	良
〃 捺印性	優	優	良
水性インク 付着性	良	良	劣
〃 捺印性	良	良	劣
堅牢性	優	優	優
耐候性	良	良	良

By adjusting appearance, it checked having the performance equivalent to the water buffalo angle which is natural material.

[0019]

[Example 2] Artificial \*\*\*\*\* \*\* W/W %\*\* \*\*\*\*\* chicken feather hair (white) impalpable powder 85.0 \*\* \*\* (black) \*\* 5.0\*\* hexamethylene di-isocyanate (HMDI) prepolymer The 10.0 total 100.0

[0020] 10 g of HMDI prepolymers were dissolved in the acetone 100g, two sorts of \*\*\*\*\* impalpable powder were thrown into this, and it was made to distribute uniformly. Acetone was promptly removed by room temperature decompression, and the surface was processed by the HMDI prepolymer in the end of a feather meal. The container made from stainless steel 100 mm in inside diameter and 50 mm in height is uniformly filled up with this end of a processing feather meal, temperature and a pressure were gradually raised with the ultra-high pressure pressing machine, by 100 \*\* and 100 ton/cm<sup>2</sup>, it held for 1 hour and compression molding was carried out. The obtained mold goods had the gloss of a translucency. This was compared with the natural tortoiseshell extracted from the hawksbill turtle.

[0021]

第 2 表

結 果

	実 施 例 2	比較例 天然べっ甲
外 観	優	優
触 感	優	優
加工性	優	優
堅牢性	優	良
耐候性	優	良

[0022] In order to process it in the shape of a striped pattern artificially, it will become possible, if laminate molding of the white of feathers impalpable powder and the black ratio is carried out so that it may differ gradually or by turns.

[0023]

[Example 3] Tire tread (keratin tire)

\*\*\* W/W %\*\* \*\*\*\*\* (beating article) 40.0. surface treatment \*\* \*\*\*\*\* powder . 20.0 \*\*\*\*\* silane coupling agent (end vinyl group). 2.0 \*\* smallness Total 62.0\*\*NR (crude rubber) 36.5\*\* sulfur 1.0\*\* rubber accelerator DPG 0.3 \*\* \*\*MBT 0.2 \*\* Total 100.0(notes)DPG(diphenylguanidine);MBT (2-mercaptobenzothiazole)

[0024]\*\* And the surface treatment of the keratin of \*\* was carried out by the silane coupling agent of \*\* diluted with ethyl acetate, and it dried. This surface treatment article was added to the compound of

\*\* - \*\*, and it kneaded by the kneader. By the WIP method (warm isostatic pressing), this kneading article was held to the tire tread for  $135 \times 8,000 \text{ kgf/cm}^2 \times 30$  minutes, and vulcanization molding was carried out to it.

[0025]The obtained mold goods were used as the even section without the pattern of 3 cm x a 5-cm angle, and the physical properties were evaluated. A contrast examination is done per same section with a commercial item 165SR13 radial-ply-tire tread part as a normal rubber tire for comparison, using a commercial item 165R13 studless tire tread part as a studless rubber tire.

[0026]

第 3 表

結 果

N o .	種 類	耐 滑 り 性 指 数	耐 摩 耗 性 指 数
1	実 施 例 (ケラチンタイヤトレッド 部)	1 9 0	8 0
2	比 較 例 (市販品165SR13 デジアルタイヤトレッド 部)	1 0 0	1 0 0

3	比 較 例 (市販品165R13 スタッドレスタイヤトレッド 部)	1 4 0	7 0
---	---	-------	-----

[0027]It examined using the slide-proof [ test-method ] sex-index constant speed method rotating-disk type frictional testing machine. Ice with the smooth surface is fixed on a rotating disc about 20 cm in diameter, a specimen (3 cm x 5 cm) is pushed on this by constant load (500g), and it is \*\*\*\*\*. The frictional force concerning a specimen when rotating a rotating disk by constant speed was detected in the load cell. A value (index) when frictional force of a comparison sample is set to 100 shows, and frictional force, i.e., slide-proof nature, is so good that a value is large.

[0028]Construction material on the surface of a rotor plate was used as asphalt, it asked from the rate of ullage (rate of abrasion proof) when carrying out fixed time rotatably operating similarly, and the value (index) when the rate of abrasion proof of the comparison sample was set to 100 showed the wear-resistant index above-mentioned test method. Abrasion resistance is so good that a value is large.

[0029]The keratin tire which consists of this examples turns into an all weather type studless tire which completely has slide resistance to all the road surfaces, such as a road surface, a snow-and-ice road surface, and an oil wetting road surface, at the time of pollution-free rain. By returning into the ground also at the time of abandonment, it becomes a good organic fertilizer and environment is hardly injured.

[Translation done.]